Steady-state and Picosecond Studies of Energy Transfer between Dyes with Closely Located S_1-Levels. Rhodamine-6G and 3,3′-Diethylthiacarbocyanine Iodide in Acetone Solution

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Lasing wavelengths and fluorescence spectra were measured for a mixed dye system containing various concentrations of Rhodamine 6G (Rh-6G) and 3,3′-diethylthiacarbocyanine iodide (DTC), which have very closely located S_1 levels, in acetone at room temperature. A new way of confirming the occurrence of energy transfer is presented on the basis of the reabsorption effect. It was found that most of the pump power absorbed by Rh-6G is transferred to DTC. A study of the fluorescence decay by a picosecond laser revealed that the energy transfer is essentially governed by the Förster mechanism. The observed fluorescence decay data agree fairly well with the R_0 value of 73.2 Å calculated from the spectral overlap.

Dye lasers have made a great progress over a wide wavelength region ranging from the ultraviolet (UV) to the infrared (IR). Hildebrand[1)] and Lin[2)] reported near-IR dye laser emission from several polymethine dyes directly pumped by UV nitrogen laser radiation (λ=337.1 nm). However, it is difficult to obtain efficient laser emission in longer wavelength regions (*e.g.*, near-IR), from nitrogen-laser pumped dye solutions, mainly because of very small absorption at 337.1 nm. A means to overcome the difficulty is the excitation of a dye laser through energy transfer processes for some dye mixture systems excited by 337.1-nm radiation of a nitrogen laser.[3—9)] The energy transfer process with the use of a proper mixture of dyes can provide a means of extending the wavelength region in which lasing is achieved.

In the dye mixture systems studied so far, the fluorescent levels of donor and acceptor are widely separated (over 1800 cm^{-1}),[3—9)] and thus there is little ambiguity in the lasing species. In a system of a donor and acceptor with closely located energy levels, however, it is difficult to identify the lasing species. Investigation of such a system seems to be important in connection with the intermolecular energy transfer in photosynthetic pigments, considering that several forms of chlorophyll with slightly different absorption maxima are operative in the primary energy-transfer process in photosynthesis.[10)] In this connection, we have studied the energy transfer mechanism. The intermolecular singlet-singlet electronic energy transfer was found to proceed by at least three mechanisms: the resonance, exchange, and trivial mechanisms.[11)] In order to differentiate various mechanisms contributing to energy transfer in dye laser systems, the study of fluorescence decay curve with a picosecond laser seems to be effective.

In this paper, we report the lasing behavior and energy transfer mechanism of the system 3,3′-diethylthiacarbocyanine iodide (DTC) as an acceptor and Rhodamine 6G (Rh-6G) as a donor in acetone at room temperature. The S_1 levels of both dyes are closely located. Some results have been reported.[12)]

Experimental

Rh-6G (laser-dye grade; Eastman Kodak Co.), DTC (laser-dye grade; Dojindo Lab.), and acetone (spectrograde or guaranteed grade) were used without further purification.

The nitrogen and dye laser system and the spectrofluorometer were constructed in our laboratory. The nitrogen laser was similar to the one described by Basting *et al.*[13)] and Maeda and Miyazoe.[14)] The dye solution in a quartz spectrofluorometer cell with a square section 1×1 cm^2 was transversely pumped by 337.1-nm radiation from a pulsed nitrogen laser with an output peak power of *ca.* 500 kW at the nitrogen pressure *ca.* 60 Torr. No mirrors were employed, lasing being conducted between the side walls of the dye cell.

The dye lasing wavelengths and fluorescence spectra were measured with a Nalumi RM-21 500-mm grating monochromator equipped with an EMI 6256S photomultiplier. For the fluorescence spectra, the sample degassed in 9 mm diam. pyrex tubes was excited by an Ushio USH-500D 500-W super-high-pressure mercury arc lamp, Toshiba V-V40 and UV-39 filters being used to select 436-nm light.[15)] For the fluorescence decay curves, the sample in a quartz spectrofluorometer cell was pumped with the second harmonic (530 nm) of a Nd^{3+}: YAG laser, the decays being measured with a Hamamatsu C979 streak camera. The donor emission was selected with a Nihon-Shinkukogaku IF-W interference filter (λ_{max}=560 nm). The time-sale of the streak camera was fully calibrated. The width of the exciting pulse was *ca.* 26 ps. The results of three shots on the same sample were averaged. All measurements were made at room temperature. Other experimental details have been reported.[9,16)]

Results and Discussion

Spectra. The absorption and fluorescence spectra of Rh-6G and DTC are shown in Fig. 1. The good spectral overlap between the Rh-6G fluorescence and DTC absorption suggests the possibility of energy transfer from Rh-6G to DTC. Since the peak wavelengths of the fluorescence spectra are close to each other for these dyes, the emission in a mixture of the two dyes can not be concluded to originate from the acceptor (DTC).

Confirmation of Energy Transfer by Reabsorption Effect. Since we observed no lasing for DTC by itself, it may follow that the excitation energy is effectively transferred from Rh-6G to DTC when the laser emission in the mixtures originates from DTC. The lasing wavelengths and fluoresence spectra of the Rh-6G-DTC dye mixture system were measured at various donor concentrations for a fixed acceptor concentration. The plot of peak wavelengths (λ_{max}) in the laser emission (L) and fluorescence (F) *versus* donor concentration [D] is shown in Fig. 2, together with the concentration dependence of the λ_{max}-values in L and F of Rh-6G alone in acetone. The λ_{max}-values in L and F of the dye mixture are independent of concentration while those in the Rh-6G only system shift to longer wavelengths with increasing concentration because of the reabsorption effect. This indicates that the emission in the dye mixture originates essentially from DTC.

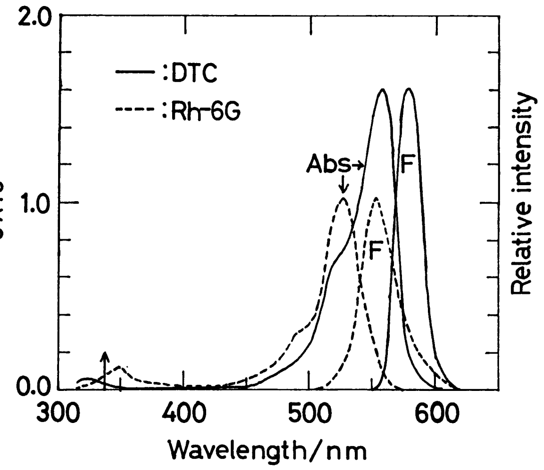

Fig. 1. Absorption (Abs) and fluorescence (F) spectra for the Rh-6G and DTC dyes separately.
Absorption path length: 1 mm. Concentration: Rh-6G, 5×10^{-5} M for Abs and 1×10^{-5} M for F; DTC, 5×10^{-5} M for Abs and 1.5×10^{-5} M for F; in acetone. The arrow on the abscissa refers to the 337.1-nm excitation wavelength.

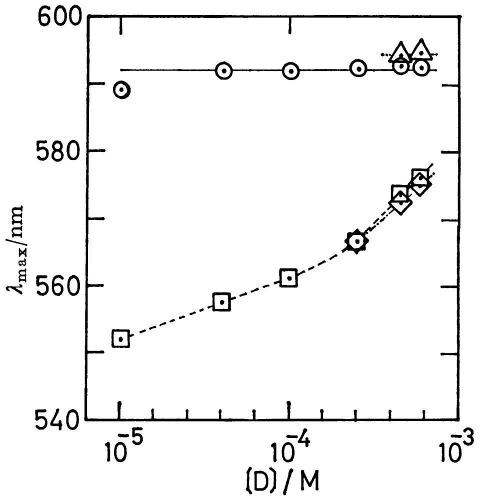

Fig. 2. Plots of the λ_{max}-values in the laser emission (L) and fluorescence (F) *versus* the Rh-6G concentration [D] for a fixed DTC concentration (1.5×10^{-4} M).
◬ and ⊙: L and F of Rh-6G-DTC dye mixture system, respectively; ◇ and ⊡: L and F of Rh-6G alone, respectively. It was not possible to obtain laser action from Rh-6G alone as well as from the mixture in the low concentration range under our experimental conditions.

We measured the λ_{max}-values of L and F in the dye mixture system at various acceptor concentrations for a fixed donor concentration. The results are shown in Fig. 3 together with the concentration dependence of λ_{max} in F of DTC in acetone. The λ_{max}-values in F of both the dye mixture and the DTC-only system agree, showing a shift due to the reabsorption effect as in the case of the Rh-6G. The λ_{max}-values in L of the dye mixture system show a concentration dependence similar to those of F mentioned above. The results show that the laser emission in the dye mixture system originates essentially from DTC at least within the concentration range studied. Most of the excitation energy absorbed by Rh-6G is transferred to DTC as a useful pump power, *viz.*, pumping by excitation transfer is efficient.

We carried out an experiment with dye mixtures containing coumarin 2 as donor and coumarin 1 as acceptor in ethanol at room temperature and at 77 K over a wide range of concentration. The S_1 levels of both dyes are more closely located than the Rh-6G-DTC system. We have confirmed on the basis of the reabsorption effect that in this system the energy transfer from coumarin 2 to coumarin 1 occurs at 77 K.[17)]

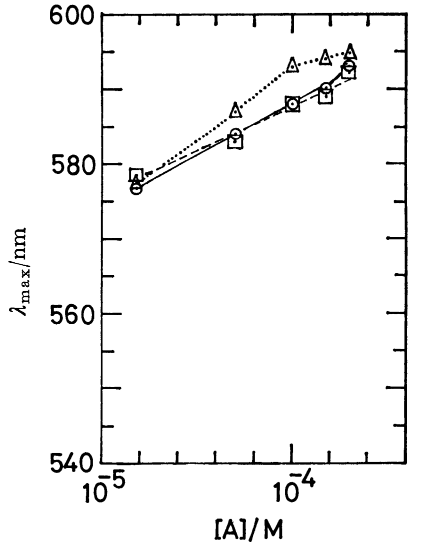

Fig. 3. Plots of the λ_{max}-values in L and F *versus* the DTC concentration [A] for a fixed Rh-6G concentration (5×10^{-4} M).
◬ and ⊙: L and F of Rh-6G-DTC dye mixture system, respectively; ⊡: F of DTC alone.

Fluorescence Decay Behavior. *Rh-6G-only and DTC-only System*: Fluorescence was monitored at 560 nm and 580 nm for Rh-6G and DTC, respectively. An exponential decay was observed in each case with lifetime of 2.6 ns (Rh-6G 1.0×10^{-5} M)[18)]† and 130 ps (DTC 2.0×10^{-6} M). The latter is in good agreement with the predicted value of Roth and Craig.[19)]

Rh-6G Plus DTC System: Fluorescence was monitored at 560 nm. The $\lambda_{\max}$-values in F of Rh-6G and DTC are 552 nm (10^{-5} M) and 590 nm (10^{-4} M), respectively. The experimental decay curves indicate that the initial part ($t\lesssim400$ ps) suffered from a serious overlap of the DTC-fluoresence. Since the initial part ($t\lesssim30$ ps) was influenced by the exciting pulse duration, only the later part of the decay was used for the analysis. The following holds for the Förster-type time-dependent fluorescence decay of the donor in the presence of a large number of acceptor molecules:[20,21)]

$$I_\mathrm{Q}(t) = I_\mathrm{Q}(0)\exp\{-t/\tau_\mathrm{D}-2([\mathrm{A}]/C_0)(t/\tau_\mathrm{D})^{1/2}\} \qquad (1)$$

where $C_0=(7.65/R_0)^3$. R_0, critical transfer distance, is given by the formula

$$R_0{}^6 = \frac{9000(\ln 10)\phi_\mathrm{D}\kappa^2}{128\pi^5 N n^4}\int f_\mathrm{D}(\bar{\nu})\varepsilon_\mathrm{A}(\bar{\nu})\mathrm{d}\bar{\nu}/\bar{\nu}^4. \qquad (2)$$

In these formulas, τ_D is the fluorescence lifetime of the donor in the absence of energy transfer, ϕ_D the fluorescence quantum yield of the donor, N Abogadro's number, n reflactive index of the media, f_D the spectral distribution of the donor fluorescence normalized to one (in units of quanta on a wavenumber scale), and ε_A the molar decadic extinction coefficient of the acceptor. The average value of κ^2, an orientation factor, is 2/3 when the molecules are free to rotate at a rate much greater than that of transfer, and 0.475[22)] when the orientation of the donor and acceptor is random but the rate of rotation is much smaller than that of transfer. From Eq. 1 and the fluorescence decay in the absence of the acceptor

$$I_\mathrm{F}(t) = I_\mathrm{F}(0)\exp(-t/\tau_\mathrm{D}), \qquad (3)$$

we have the linear relationship:

$$\ln[I_\mathrm{Q}(t)/I_\mathrm{F}(t)] = \ln[I_\mathrm{Q}(0)/I_\mathrm{F}(0)]-2([\mathrm{A}]/C_0)\tau_\mathrm{D}{}^{-1/2}t^{1/2}. \qquad (4)$$

The values of C_0 and R_0 can be calculated from the spectral overlap of fluorescence band of Rh-6G and absorption band of DTC to be 1.14×10^{-3} M and 73.2 Å, respectively. The value of the orientation factor κ^2 was assumed to be 2/3 in this calculation (*vide infra*). In Fig. 4, $\ln[I_\mathrm{Q}(t)/I_\mathrm{F}(t)]$ is plotted against $t^{1/2}$, the number of data points being restricted for the sake of clarity. The straight line in the figure has the slope calculated with the values given above. The experimental points representing the later part of decay seem to fit the line although the data points are scattered because of the small intensity of $I_\mathrm{Q}(t)$. This suggests that the energy transfer in the present dye laser system takes place essentially through the process of nonradiative resonance transfer of the Förster type. A large R_0 value is due to a large spectral overlap, which is in turn caused by the closely located S_1 levels of the dyes.

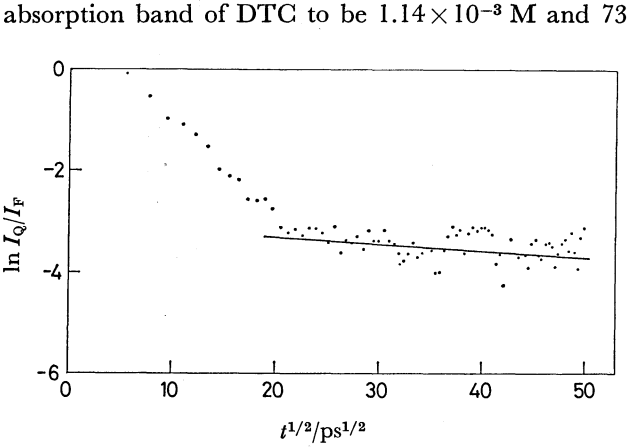

Fig. 4. $\ln[I_\mathrm{Q}(t)/I_\mathrm{F}(t)]$ plotted as a function of $t^{1/2}$. $I_\mathrm{Q}(t)$: Rh-6G 1×10^{-5} M, DTC 9×10^{-5} M, $I_\mathrm{F}(t)$: Rh-6G 1×10^{-5} M. The slope of the straight line was calculated with $R_0=73.2$ Å.

The Förster theory assumes that the rate of translational diffusion is small enough to preclude a significant perturbation of the random distribution of distances between D and A during the course of measurement.[11d,11e)] On the basis of picosecond-absorption spectroscopic studies Rehm and Eisenthal[23)] stated that the Förster theory gives a good description of singlet-singlet energy transfer between Rh-6G (donor) and malachite green (acceptor) in glycerol even up to the earliest time (20 ps). Porter and Tredwell[21)] carried out similar studies with a picosecond laser and streak camera system on the same pair in a low viscosity solvent (ethanol), showing that the Förster theory is applicable up to a limiting time resolution of 10 ps. They showed that translational diffusion does not distort the kinetics of the energy transfer system at a viscosity of 1.2 cP.†† The significant changes in the intermolecular distances during energy transfer can be precluded because of the relationship[11c)]

$$R_0 \gg [2(D_\mathrm{D}+D_\mathrm{A})\tau_\mathrm{D}]^{1/2}, \qquad (5)$$

where D_D and D_A are the diffusion coefficients of the donor and acceptor, respectively. In our case, the viscosity of the solvent (0.32 cP) is *ca.* 4-fold smaller than in their case; the diffusion coefficient of Rh-6G would be *ca.* 4 times larger, assuming the Stokes-Einstein relation $D=kT/(6\pi\eta b)$.[11b)] The coefficient for DTC is unknown. However, the size and charge of the molecule are comparable to those of Rh-6G indicating that the value of the coefficient should be similar. Thus, $[2(D_\mathrm{D}+D_\mathrm{A})\tau_\mathrm{D}]^{1/2}$ would be *ca.* 45 Å, twice as large as in the case of Porter and Tredwell. Our value of R_0, 73.2 Å is much larger.

Gösele *et al.*[24)] reported that an expression formally analogous to Eq. 1 can be obtained for the time-dependent fluorescence intensity even when diffusion governs the fluorescence quenching effects. In the diffusion-governed kinetics, instead of $R_0{}^3$, should be used $r_\mathrm{AD}^2 D^{1/2}\tau_\mathrm{D}^{1/2}$ multiplied by a constant with a value close to 2, where r_AD is a certain collision distance and D the sum of D_A and D_D (the quantity α in their formulas is replaced by R_0^6/τ_D). According to these authors, the quenching effects are controlled by diffusion and by long-range energy transfer when $Z_0=R_0^3/(2r_\mathrm{AD}^2D^{1/2}\tau_\mathrm{D}^{1/2})\ll1$ or $Z_0\gg1$, respectively. For the case where the long-range energy transfer is

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† 1 M=1 mol dm^{-3} in this paper,

†† 1 cP=10^{-3} kg m^{-1} s^{-1} in SI units,

dominant, we have $R_0 \gg r_{AD}$ and hence $R_0^2 \gg 2^{1/2} r_{AD}^2$. When we multiply the left and right sides of the inequality 5 by R_0^2 and $2^{1/2} r^2{}_{AD}$ respectively, we obtain the relation $Z_0 \gg 1$. Thus, the relation $Z_0 \gg 1$ is equivalent to inequality 5.

Birks[11c] and Birks and Georghiou[25] observed the donor fluorescence decay of phenanthrene in the absence and presence of acridine in six solvents of viscosity $\eta = 64.6$ cP (cyclohexanol) to 0.4 cP (heptane). Their results were compared with the relations of Förster[20], Yokota and Tanimoto[26], and Voltz *et al.*,[27] the last being developed from diffusion theory and extrapolates to Stern-Volmer kinetics.[11c] A mean value of $R_0 = 25.5$ Å was obtained from the spectroscopic data. At $\eta = 64.6$ cP, where $\sqrt{2D\tau_D} < R_0$, the donor decay follows Förster kinetics. At $\eta < 3.7$ cP where $\sqrt{2D\tau_D} > 3R_0$, the decay was exponential, following Stern-Volmer kinetics. At intermediate viscosities, where the decay was non-exponential but more rapid than predicted by the Förster relation, the decay agreed with the Yokota-Tanimoto relation within experimental error. The Voltz relation predicted a more rapid decay than that observed.

In our case, R_0 is much larger than $\sqrt{2D\tau_D}$. In the Yokota-Tanimoto relation, the second term in the exponent of Eq. 1 is multiplied by

$$B = [(1 + 10.87x + 15.50x^2)/(1 + 8.743x)]^{3/4} \tag{6}$$

with $x = D\alpha^{-1/3} t^{2/3} = D R_0^{-2} \tau_D^{1/3} t^{2/3}$. The slope of the $\ln[I_Q(t)/I_F(t)]$ *vs.* $t^{1/2}$ plot is not constant but dependent on $t^{1/2}$ because of the presence of B. For our case with $D = 1 \times 10^{-5}$ cm^2 s^{-1}, $R_0 = 73.2$ Å, and $\tau_D = 2.6$ ns, the slope calculated by means of the Yokota-Tanimoto relation increases in absolute value with $t^{1/2}$. The experimental points in Fig. 4 show no such tendency. The slope is constant and time-independent, indicating that the Förster kinetics is applicable, although the viscosity of the solvent is very low. If we compare our results with those of Birks and Georghiou,[25] we find the following: (1) a larger R_0 value, $R_0 = 73.2$ Å instead of 25.5 Å, (2) a larger b value, large dye molecules instead of small molecules phenanthrene and acridine and (3) a smaller τ_D value, $\tau_D = 2.6$ ns instead of $\tau_D \approx 60$ ns. Each of the effects (1), (2), and (3) diminishes the boundary value of η for diffusion-dominated kinetics, *i.e.*, a value of η which satisfies $\sqrt{2D\tau_D} = 3R_0$. The value becomes smaller by a factor of $(73.2/25.5)^2 \approx 8$ than that of Birks and Georghiou if we take (1) into consideration.

The energy transfer seems to follow the Förster mechanism, although some contribution of diffusion controlled process can not be entirely ruled out.

Bojarski and Dudkiewicz[28] proposed the concentration effects on orientation factor κ^2 by considering the concentration-dependent ratio of rotation time (τ_r) and time of the excitation energy localization $\tau_1 = [\sum\limits_{D} k_{D^*D} + \sum\limits_{A} k_{D^*A} + k_F + k_q]^{-1}$, where k_{D^*D} and k_{D^*A} denote the rate constant of long-range nonradiative electronic excitation energy transfer due to the dipole-dipole interaction between an excited donor (D*) and an unexcited donor (D) and that between D* and an acceptor (A), respectively, and k_F and k_q those for emission and internal conversion, respectively. They assumed the value of κ^2 to be a function of $a = \tau_r/\tau_D$ and $\gamma = [A]/C_0$. The deviation of κ^2 from the value of rapid rotation is important when $\gamma \geq 1$ for $a \leq 0.1$. For a larger a, it becomes prominent from a smaller γ. They reexamined the data of Porter and Tredwell[21] and concluded that the small systematic change in C_0 can be caused by the change in κ^2. In the case (P. and T.) ($\tau_r = 320$ ps. $\tau_D = 4200$ ps, $a = 0.0762$) the acceptor concentration is very high (10^{-2}—10^{-3} M), the values of γ being in the range 3.05—0.33. In our case, the value of τ_r should be smaller than that in more viscous ethanol (320 ps). With $\tau_D = 2600$ ps, the value of a would be *ca.* 0.1. Since $\gamma = 9 \times 10^{-5}/1.14 \times 10^{-3} = 0.079$, the deviation of the value of κ^2 from the value of rapid rotation can be neglected. The value $\kappa^2 = 2/3$ seems to be reasonable.

Concluding Remarks. A new method has been worked out for confirming the occurrence of energy transfer on the basis of the reabsorption effect. Rh-6G, with a high fluorescence quantum yield (0.83 or 0.92)[18] and a good spectral overlap characteristics with DTC, can be used as an efficient donor for lasing of DTC even though DTC has a very low fluorescence quantum yield (0.048).[19] The energy transfer occurs by a nonradiative process of the Förster-type. French *et al.*[10] found that the absorption bands of chloroplasts can be considered as a superposition of bands associated with several chlorophyll forms. A very efficient energy transfer occurs among them, their S_1 levels being very close. The dyes we used have very closely located S_1 levels. A combination of these dyes can be considered as a model system of chloroplasts. Occurrence of resonance energy transfer is possible for these dyes even in dilute solutions (below 10^{-3} M) mainly due to good spectral overlap characteristics, *i.e.*, a large value of R_0. Further experiments on the energy transfer of these dyes in micellar systems are in progress.[29–30]

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